Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2022, **32**, 478–481

Mendeleev Communications

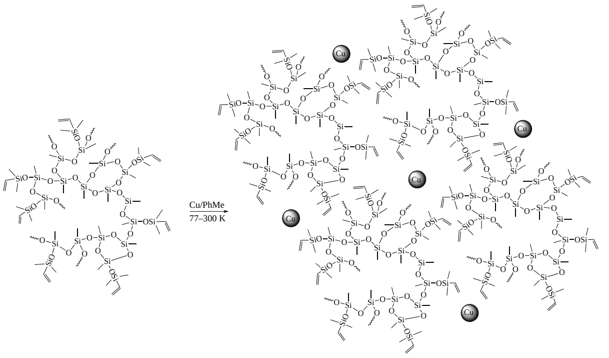
Copper-containing polymethylsilsesquioxane nanocomposites in catalytic olefination reaction

Alexander Yu. Vasil'kov,[a] Dmitry A. Migulin,*[b] Vasiliy M. Muzalevskiy,[c] Alexander V. Naumkin,[a] Alexander Yu. Pereyaslavtsev,[d] Yan V. Zubavichus,[e] Valentine G. Nenajdenko[c] and Aziz M. Muzafarov[a,b]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[b] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation. E-mail: migulinda@ispm.ru*
[c] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[d] *Dukhov Automatics Research Institute, 127030 Moscow, Russian Federation*
[e] *Synchrotron Radiation Facility 'SKIF', Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630559 Kol'tsovo, Russian Federation*

DOI: 10.1016/j.mencom.2022.07.016

New copper-containing organosilicon hybrid materials were synthesized by the reaction of branched polymethylsilsesquioxane with copper nanoparticles prepared by the metal-vapor synthesis. Hybrid materials showed a high activity in the catalytic olefination of *p*-chlorobenzaldehyde hydrazone with polyhaloalkanes such as $CBrCl_3$, CBr_4 and CF_3CBr_3 to afford the corresponding halostyrenes in the yields above 80%. The structure and composition of the prepared nanocomposites were studied by X-ray using synchrotron radiation to show that the active sites of the catalysts are mixed copper(I)–copper(II) oxides (Cu–Cu_2O–CuO) in nature.



Keywords: copper nanoparticles, polymethylsilsesquioxane, catalytic olefination, metal-vapor synthesis, hydrazones, *p*-chlorobenzaldehyde, polyhaloalkanes, halostyrenes.

Catalytic olefination reaction (COR) is a convenient tool for the synthesis of alkenes, based on the transformation of carbonyl compound hydrazones upon treatment with polyhaloalkanes in the presence of a base (usually ammonia or ethylenediamine) and catalytic amounts of copper salts. The reaction has a broad scope affording alkenes with various combinations of the substituents at the double bond.[1] The reaction can be performed using pre-synthesized hydrazones[2] or hydrazones prepared *in situ*.[3] Using fluorinated polyhaloalkanes opens a way to fluorinated alkenes[1] being valuable building-blocks for the synthesis of various fluorinated compounds by reactions with nucleophiles and heterocyclizations.[4,5] Since COR requires the presence of copper catalyst to proceed efficiently, searching for novel efficient copper-derived catalysts is an important task.

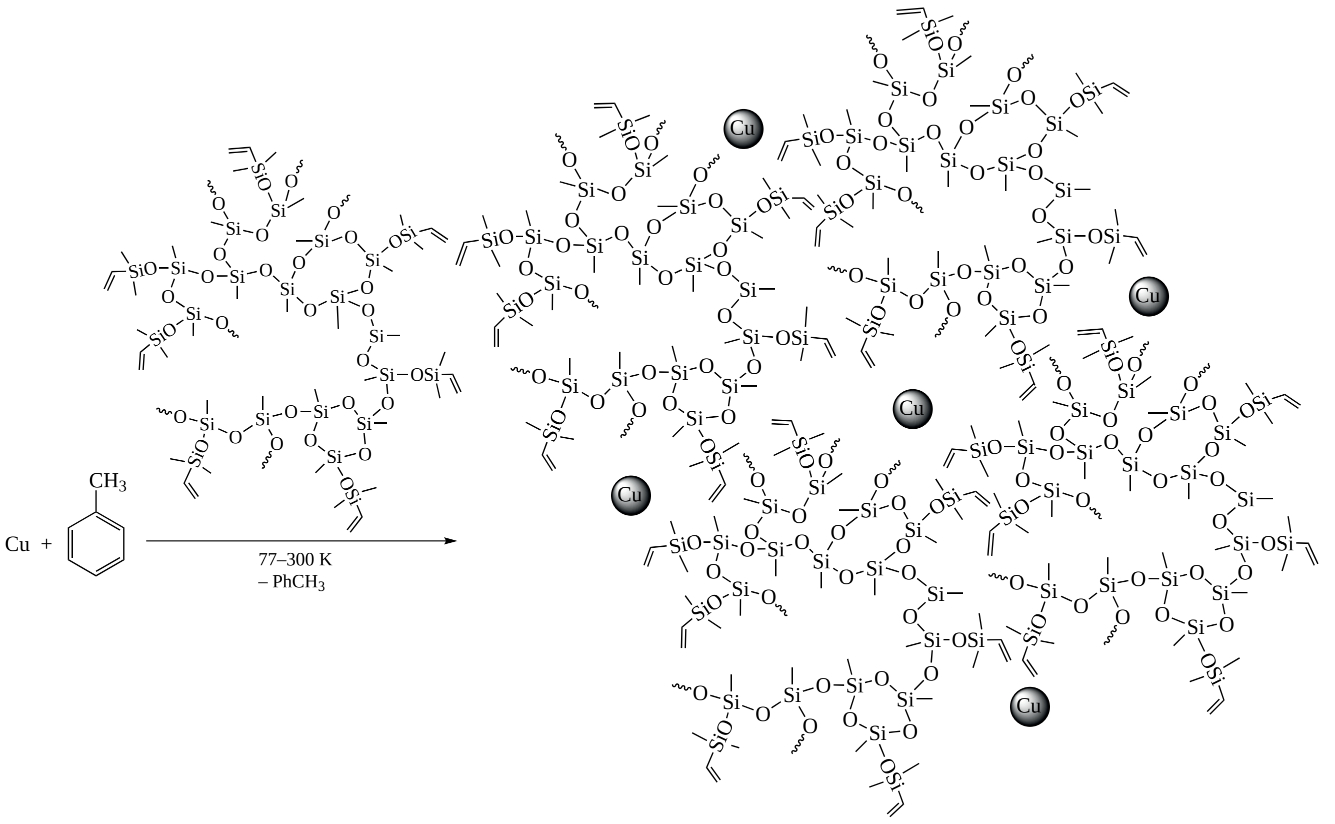
There is currently a stable interest to hybrid catalysts with an active metal-containing component immobilized in a mesoporous polymeric matrix. The activity of such systems is often governed by peculiar active component–matrix interaction effects.[6–11] Metal-modified oligomeric and polymeric siloxanes occupy a special place among these composites. Numerous molecular cage-like metallosiloxanes of variable nuclearity and their catalytic properties are documented.[12–14]

Nanogels based on branched organosilicon polymers are another promising type of supports for catalytically active metal nanoparticles. They enable catalytic reactions to proceed under conditions intermediate between homogeneous and heterogeneous modes. The use of such hybrid materials in particular can be a promising route to design catalysts with improved performance characteristics towards olefination reactions.

Copper-based nanostructured species prepared by metal-vapor synthesis (MVS)[15–19] in the form of organosols or supported on metal oxides were effective in dimerization of haloarenes (the Ullmann reaction[15]), phenol oxidation[20] and partial oxidation of cyclohexane.[21] Heterogeneous catalysts prepared by MVS containing Cu, Ag, and Au nanoparticles demonstrated activity in the catalytic olefination as well.[22] Branched organosilicon polymers are thermally stable,[23–25] resistant to oxidation and are promising for the creation of hybrid materials containing metal nanoparticles with catalytic, magnetic and other functional properties.[26,27]

In this paper, we present the synthesis of a new hybrid material of Cu-containing organosilicon nanogel and a study of its COR activity. Polymethylsilsesquioxane (PMSSO) nanogel with a core–shell structure in which functional vinyl groups form the shell of the macromolecule was used as the organosilicon polymer.[28] The catalytically active nanocomposite Cu-polymethylsilsesquioxane (Cu/PMSSO-VDMS) **1** was prepared by a modification of polymer support based on PMSSO capped with TMDVDS (PMSSO-VDMS) with copper nanoparticles produced *via* the metal-vapor synthesis (Scheme 1, for details see Online Supplementary Materials).

The use of an organosilicon nanogel as a matrix stabilizing metal nanoparticles makes it possible to obtain a nanocomposite



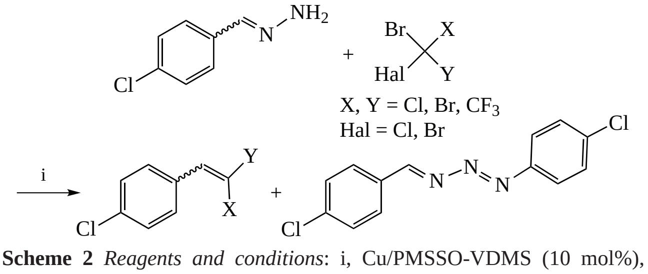
Cu/PMSSO-VDMS **1**

Scheme 1

1 which is close in its structure to microheterogeneous metal complex catalysts. In these systems, the size and electronic state of metal are largely determined by the reaction conditions and the nature of the interaction of nanoparticles with functional groups of polymers. By changing the nature of the functional groups in the nanogel it is possible to influence the structure of the resulting metallopolymers. The search for new effective catalysts for olefination reactions is of importance due to the possibility of using this process for a wide variation of the nature of the substituent at the double bond, and X-ray absorption spectroscopy is indeed the technique of choice to probe the balance of charge states in the bulk of the porous catalyst.[29,30]

The activity of the resulting material, Cu-containing polymethylsilsesquioxane nanogel (Cu/PMSSO-VDMS), was investigated in COR involving *p*-chlorobenzaldehyde hydrazone and three polyhaloalkanes $CBrCl_3$, CBr_4, and CF_3CBr_3 using the standard procedure (Scheme 2, for more details, see Online Supplementary Materials). In this way, various halostyrenes were obrained.

It was found that Cu-containing nanogel presents a promising alternative (or additional option) to the traditional copper catalysts used in COR. Thus, the reaction of *p*-chlorobenzaldehyde hydrazone with $CBrCl_3$, CBr_4 and CF_3CBr_3 led to the corresponding substituted alkenes in 86, 82 and 83% yields, respectively. It should be noted that these values are about 5–10% higher than those in case of traditional catalysts for COR. This fact can be explained by more optimal rate of the reaction. In the case of traditional homogeneous copper catalysts, the reaction proceeded within few minutes which led to a quite fast heat evolution and local overheating. In contrast, for full transformation of *p*-chlorobenzaldehyde hydrazone several hours were needed in case of Cu-containing nanogel. Obviously, local overheating is not possible under such circumstances, which provides higher yields of halostyrenes.



Scheme 2 *Reagents and conditions*: i, Cu/PMSSO-VDMS (10 mol%), NH_3 (aq.), DMSO, room temperature, 12 h.

The Cu nanoparticles can initiate similar processes. The catalytic activity of Cu nanoparticles with an average size of about 3.6 nm prepared by MVS in the reaction of phenol oxidation in methanol was studied previously.[15] In the products of the reaction carried out at 298 K and 1 atm O_2, 4,5-dimethoxy-1,2-benzoquinone and other oxygen-containing compounds were observed. The authors attribute the catalytic effect to the formation of an active layer with chemisorbed oxygen on the surface of Cu nanoparticles, which facilitates the oxidation of organic compounds.

The obtained results made it possible to evaluate the activity of Cu-containing nanogels in the catalytic reaction. The efficiency of catalysts in COR turned out to be comparable or higher than that of heterogeneous systems obtained earlier by the MVS method as in the case of Cu/SiO_2.[22] Thus, when using $CBrCl_3$, the yield of the main product for described here Cu/PMSSO-VDMS **1** and earlier reported Cu/SiO_2 are 86 and 81%, respectively.

To shed light onto the chemical nature of active sites in the Cu-containing nanocomposite **1**, XPS and Cu K-edge XANES/EXAFS instrumental techniques were applied. In the survey photoelectron spectrum of the Cu/PMSSO composite **1**, peaks characteristic of Cu, Si, O, and C atoms are recorded. A quantitative analysis shows the composition to be $Cu_{6.8}Si_{22.5}C_{35.8}O_{35.0}$. The C 1s photoelectron spectrum of the

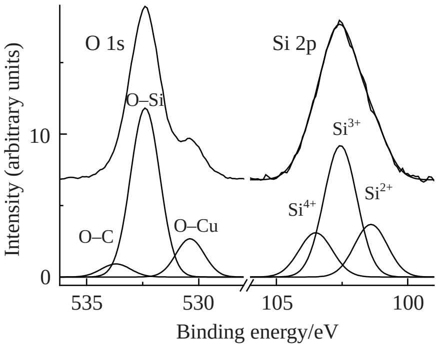


Figure 1 Photoelectron O 1s and Si 2p spectra of the Cu/PMSSO composite **1**.

Cu/PMSSO system **1** is described by three components. Most of the carbon atoms correspond to the C–Si bonds (~95%) at 284.5 eV, the fraction of carbon atoms bound to oxygen is about 5% and can be attributed to the C–OH and/or C–O–C components at 286.0 eV and C=O at 287.4 eV. The C 1s spectrum lacks signals at 284.1 eV, which is characteristic of the vinyl bond,[31] and the satellite in the region of 291.5 eV, which corresponds to olefins. This may be due to the opening of the olefin bond and its possible partial polymerization or with the formation of oxygen-containing fragments.

The O 1s spectrum (Figure 1) was fitted with three peaks at 530.3, 532.3 and 533.6 eV with Gaussian widths of 1.25, 1.3 and 1.3 eV which correspond to the Cu–O, Si–O and C–O bonds with relative intensities of 0.17, 0.77 and 0.06, respectively.

The Si 2p spectrum of **1** (see Figure 1) is approximated with three peaks at 101.3, 102.5 and 103.4 eV with the same peak widths of 1.25 eV. The binding energies correspond to Si^{2+}, Si^{3+} and Si^{4+} states. Such a structure of the spectrum is due to the variety of possible chemical bonds, such as –Si–O–, –Si–OO–, –Si–O–Si–O– and others, in which a noticeable effect of oxygen-containing polymer fragments on the electron density at Si atoms and the corresponding chemical shifts is manifested.

Figure 2 shows the Cu 2p photoelectron spectrum of the copper-containing nanogel. Binding energies of 932.0 and 951.8 eV related to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks correspond to the Cu^+ state.[32] This result is consistent with fitting the O 1s spectrum that shows a peak at 530.3 eV assigned to the Cu–O bond. Kinetic energy of $L_3M_{45}M_{45}$ Auger peak (916.8 eV), its line shape and Auger parameter (1848.8 eV) are characteristic of Cu^+ state as well.[33] According to the NIST XPS database,[33] binding energies of Cu $2p_{3/2}$ peak and Auger parameters Cu $2p_{3/2} + L_3M_{45}M_{45}$ of Cu, Cu_2O and CuO are in the ranges of 932.62, 932.0–932.8, 933.2–934.6 eV and 1851.3, 1848.6–1849.6, 1850.7–1852.0, respectively. It should be noted that 932.62 and 1851.3 eV are recommended values.[34]

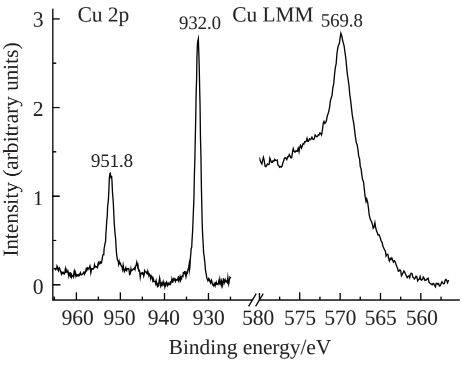


Figure 2 Photoelectron Cu 2p and Cu LMM Auger spectra of Cu/PMSSO composite **1**.

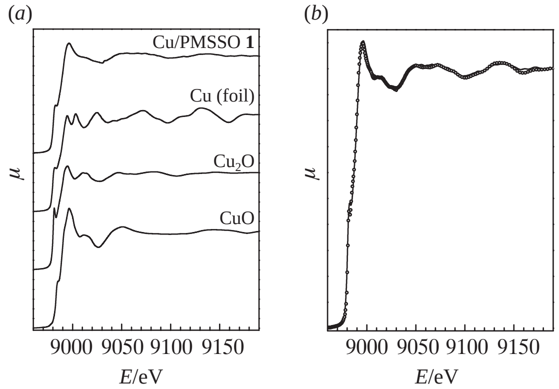


Figure 3 (*a*) Experimental XANES spectra at the K-edge of copper of the catalyst **1** and the spectra of reference copper compounds and (*b*) the result of modeling the experimental spectrum of the composite with a linear combination of reference spectra corresponding to the formal composition 24% Cu + 45% Cu_2O + 31% CuO (the linear combination is shown by circles).

A comparative analysis of the structural formula of the nanogel with the XPS quantification data for a copper-containing composite showed that the measured O/Si ratio exceeds the theoretical one by a factor of ~1.5, while the corresponding C/Si ratio differs insignificantly. Apparently, this may indicate a considerable amount of formed –Si–O–O–Si bonds in the nanocomposite.

Also, for the Cu-containing catalyst **1**, X-ray absorption spectra (XANES/EXAFS) were recorded at the K-edge of copper (Figure 3).

The chemical state of copper atoms in the composite does not exactly coincide with any of the measured reference samples. Apparently, this means that the composite contains a set of nonequivalent states. Using the method of linear combination of reference spectra, the experimental spectrum of the composite was approximated by the combination of 24% Cu + 45% Cu_2O + + 31% CuO. The results of the analysis of the EXAFS spectra are shown in Figure 4 and in Table S1 (see Online Supplementary Materials). In the local environment of copper atoms, two maxima corresponding to the contributions of Cu–O and Cu–Cu dominate, which is in agreement with preliminary conclusions from the XANES data. The best agreement between the theoretical and experimental curves is achieved when two Cu–Cu distances of 2.51 and 2.71 Å are included in the structural model. The quantitative discrepancy in the assessment of the content of various states of copper in the XPS and XANES/EXAFS nanocomposite is due to the difference in their information depth when the first is surface-sensitive while the second is bulk-sensitive.

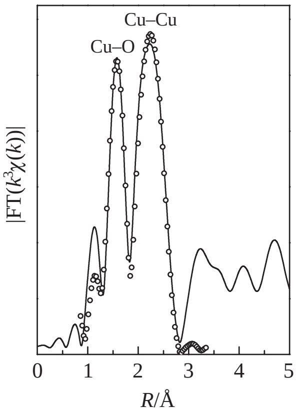


Figure 4 Fourier transform of the experimental XANES spectrum at the K-edge of copper for the Cu/PMSSO composite (solid line) and the optimized theoretical curve (circles).

In conclusion, a technique for obtaining new hybrid materials based on organosilicon nanogels modified with copper nanoparticles has been developed. Copper-containing nanogels exhibited high activity in the reaction of catalytic olefination, which shows that this synthetic approach is promising for producing new functional materials. The essential difference between these nanogels and the previously described systems is that the proposed synthetic method allows one to effectively stabilize copper nanoparticles already formed under MVS conditions in an organosilicon matrix without loss of catalytic activity. This opens the possibility, by varying the nature of the functional groups of the nanogel which interact with the metal surface, to control the electronic state of the metal, and, hence, the catalytic properties of the system as a whole.

This work was supported by the Russian Science Foundation (grant no. 21-13-00437). XPS studies were performed with the financial support of the Ministry of Science and Higher Education of the Russian Federation (contract no. 075-00697-22-00) employing the equipment of Center for molecular composition studies of INEOS RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.016.

References

1 V. G. Nenajdenko, V. M. Muzalevskiy and A. V. Shastin, *Chem. Rev*., 2015, **115**, 973.
2 A. V. Shastin, V. N. Korotchenko, V. G. Nenaidenko and E. S. Balenkova, *Russ. Chem. Bull.*, 1999, **48**, 2184 (*Izv. Akad. Nauk, Ser. Khim*., 1999, 2210).
3 V. G. Nenajdenko, A. V. Shastin, V. M. Muzalevskii and E. S. Balenkova, *Russ. Chem. Bull.*, 2004, **53**, 2647 (*Izv. Akad. Nauk, Ser. Khim*., 2004, 2538).
4 V. M. Muzalevskiy, *Chem. Heterocycl. Compd.*, 2012, **48**, 117 (*Khim. Geterotsikl. Soedin*., 2012, **48**, 122).
5 E. S. Balenkova, A. V. Shastin, V. M. Muzalevskiy and V. G. Nenajdenko, *Russ. J. Org. Chem*., 2016, **52**, 1077 (*Zh. Org. Khim*., 2016, **52**, 1087).
6 Q. Chang, J. H. Lee, Y. Liu, Z. Xie, S. Hwang, N. S. Marinkovic, A.-H. A. Park, S. Kattel and J. G. Chen, *JACS Au*, 2022, **2**, 214.
7 Z. Wu, X. Zhang, E. D. Goodman, W. Huang, A. R. Riscoe, S. Yacob and M. Cargnello, *ACS Catal*., 2020, **10**, 9356.
8 S. Kramer, N. R. Bennedsen and S. Kegnæs, *ACS Catal*., 2018, **8**, 6961.
9 K. Wang, L. Yang, W. Zhao, L. Cao, Z. Sun and F. Zhang, *Green Chem.*, 2017, **19**, 1949.
10 S. Thanneeru, S. S. Duay, L. Jin, Y. Fu, A. M. Angeles-Boza and J. He, *ACS Macro Lett*., 2017, **6**, 652.
11 I. S. Borisov, D. Yu. Mladentsev, B. A. Guzeev, G. P. Goryunov, D. V. Uborsky, A. Vittoria, R. Cipullo, V. Busico, N. Friederichs and A. Z. Voskoboynikov, *Mendeleev Commun*., 2020, **30**, 449.
12 M. M. Levitsky, B. G. Zavin and A. N. Bilyachenko, *Russ. Chem. Rev.*, 2007, **76**, 847 (*Usp. Khim*., 2007, **76**, 885).
13 M. M. Levitsky, A. I. Yalymov, A. N. Kulakova, A. A. Petrov and A. N. Bilyachenko, *J. Mol. Catal. A: Chem.*, 2017, **426**, 297.
14 M. M. Levitsky, Y. V. Zubavichus, A. A. Korlyukov, V. N. Khrustalev, E. S. Shubina and A. N. Bilyachenko, *J. Clust. Sci.*, 2019, **30**, 1283.
15 A. A. Ponce and K. J. Klabunde, *J. Mol. Catal. A: Chem.*, 2005, **225**, 1.
16 G. Cardenas-Trivino, C. Elgueta, L. Vergara, J. Ojeda, A. Valenzuela and C. Cruzat, *Int. J. Biol. Macromol*., 2017, **104**, 498.
17 S. P. Bhaskar and B. R. Jagirdar, *J. Chem. Sci.*, 2012, **124**, 1175.
18 S. B. Kalidindi and B. R. Jagirdar, *J. Phys. Chem. C*, 2008, **112**, 4042.
19 A. B. Smetana, K. J. Klabunde, C. M. Sorensen, A. A. Ponce and B. Mwale, *J. Phys. Chem. B*, 2006, **110**, 2155.
20 G. Vitulli, M. Bernini, S. Bertozzi, E. Pitzalis, P. Salvadori, S. Coluccia and G. Martra, *Chem. Mater*., 2002, **14**, 1183.
21 C. Evangelisti, G. Vitulli, E. Schiavi, M. Vitulli, S. Bertozzi, P. Salvadori, L. Bertinetti and G. Martra, *Catal. Lett*., 2007, **116**, 57.
22 V. G. Nenajdenko, A. Yu. Vasil'kov, A. A. Goldberg, V. M. Myzalevskiy, A. V. Naumkin, V. L. Podshibikhin, A. V. Shastin and E. S. Balenkova, *Mendeleev Commun*., 2010, **20**, 200.
23 G. Hayase, K. Kanamori and K. Nakanishi, *Microporous Mesoporous Mater*., 2012, **158**, 247.
24 W. Zheng, J. Xie, J. Zhang, C. Tang and Z. Zhao, *Materials*, 2018, **11**, 2317.
25 M. A. Obrezkova, I. I. Saraeva, G. M. Ignat'eva, N. G. Vasilenko and A. M. Muzafarov, *Mendeleev Commun.*, 2021, **31**, 704.
26 A. Yu. Vasil'kov, D. A. Migulin, A. V. Naumkin, O. A. Belyakova, Ya. V. Zubavichus, S. S. Abramchuk, Yu. V. Maksimov, S. V. Novichikhin and A. M. Muzafarov, *Mendeleev Commun*., 2016, **26**, 187.
27 C. Gao and D. Yan, *Progr. Polym. Sci*., 2004, **29**, 183.
28 D. Migulin, E. Tatarinova, I. Meshkov, G. Cherkaev, N. Vasilenko, M. Buzin and A. Muzafarov, *Polym. Int*., 2016, **65**, 72.
29 A. Balerna, C. Evangelisti and C. Tiozzo, *X-Ray Spectrom*., 2017, **46**, 82.
30 M. Marelli, A. Jouve, A. Villa, R. Psaro, A. Balerna, L. Prati and C. Evangelisti, *J. Phys. Chem. C*, 2019, **123**, 2864.
31 M. Ahsani, R. Sabouri, M. Ulbricht, H. Hazrati, A. Jafarizad and R. Yegani, *J. Appl. Polym. Sci*., 2021, **138**, 50977.
32 R. P. Vasquez, *Surf. Sci. Spectra*, 1998, **5**, 257.
33 *NIST X-ray Photoelectron Spectroscopy Database*, *Version 4.1*, National Institute of Standards and Technology, Gaithersburg, 2012, http://srdata.nist.gov/xps.
34 C. J. Powell, *J. Electron. Spectrosc. Relat. Phenom.*, 2012, **185**, 498.

Received: 13th December 2021; Com. 21/6772